Comment on "Nonanalyticity of the optimized effective potential with finite basis sets"

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In a recent paper [Phys. Rev. A **85**, 052508 (2012)], Gidopoulos and Lathiotakis discuss difficulties in solving the optimized effective potential (OEP) equation in a finite basis. We show that these difficulties are resolved by choosing basis sets that fulfill a balance condition. In particular, the nonanalyticity of the finite-basis OEP equation disappears in basis-set convergence. In connection with the basis-set balance, we also discuss the role of small eigenvalues. The approximate treatment of them with a common energy denominator suggested by the authors requires care in order to avoid spurious oscillations in the potential. We briefly discuss an alternative scheme that overcomes the aforementioned difficulties and enables OEP calculations with a minimal orbital basis.

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I. INTRODUCTION

Recently, Gidopoulos and Lathiotakis analyzed the construction of the local effective potential in the optimized effective potential (OEP) method using finite basis sets [1]. Central to the paper is a proof that the potential obtained as a solution of the OEP equation can be nonanalytic [2] in terms of a parameter λ that connects the finite-basis solution ($v^{\lambda=0}$) with the exact one ($v^{\lambda=1}$), succinctly expressed in the conclusions: "The full OEP is part of the family of OEPs v^{λ} that is separated from v^0 by a discontinuous jump." This assertion calls for a rapid clarification since it casts doubt on many numerical OEP calculations that have been performed using finite basis sets in recent years [3–11].

In this Comment, we show that the nonanalyticity disappears if the basis-set convergence is performed with basis sets that fulfill a balance condition, a requirement that has been identified and has been explained in a number of earlier papers [12–20] (and has been used in the calculations cited above). In this sense, the nonanalyticity is rather a measure of the quality of the orbital basis than anything fundamental.

When established, the basis-set balance tends to avoid small eigenvalues in the density response matrix χ [19,20], an observation that is backed up by fundamental considerations based on the homogeneous electron gas. Otherwise, the solution of the OEP equation would involve the inversion of a nearly singular matrix. We, therefore, suspect that the unphysically small eigenvalues of χ shown in Fig. 1 of Ref. [1] result from an underconverged orbital basis. The authors eliminate these small eigenvalues from χ in order to separate off its so-defined *null space*, which is treated later in an approximate way. However, the resulting potentials can still show sizable oscillations, which we attribute to the inadequate (i.e., only approximate) treatment of the null space: The small eigenvalues are counterbalanced in the OEP equation by equally small values of the response of the exchange energy, giving rise to nonsingular and often physically important contributions to the OEP.

After setting the stage by defining several quantities, we explain what the condition of basis-set balance is and why it must be fulfilled in OEP calculations. Then, we show, for the case of diamond bulk, a systematic convergence of the OEP as an illustration. Thanks to the basis-set balance, our potentials show no sign of unphysical oscillations. We also prove that the potential $v^{\lambda}(\mathbf{r})$, as it is defined in Ref. [1], becomes analytic if the basis-set convergence is taken in balance, revealing the nonanalyticity to be indicative of underconverged basis sets. Additionally, we discuss the role of small eigenvalues of the density response function, which can appear as a result of unbalanced basis sets. Finally, we comment on how OEP calculations can be made more efficient.

II. DEFINITIONS

Unless noted otherwise, we use the definitions of Ref. [1]. The OEP formalism was applied to the exact exchange energy functional, where correlation energy contributions are neglected. The OEP $v(\mathbf{r})$ is defined as the potential stemming from the electron-electron interaction, i.e., it consists of the Hartree potential $v_{\mathrm{H}}(\mathbf{r})$ and the local exchange potential $v_{\mathrm{x}}(\mathbf{r})$. Since the former is given as a known functional of the electron density $n(\mathbf{r})$, one usually solves the OEP equation only for $v_{\mathrm{x}}(\mathbf{r})$. However, a solution for the full potential $v(\mathbf{r}) = v_{\mathrm{H}}(\mathbf{r}) + v_{\mathrm{x}}(\mathbf{r})$ is mathematically equivalent, and this is the approach chosen in Ref. [1].

We consider two sets of basis functions, a basis for the orbitals $\phi_i(\mathbf{r})$ and an auxiliary basis $\{\xi_k(\mathbf{r})\}$, which is assumed orthonormal here for simplicity, for representing the potential $v(\mathbf{r})$ [or $v_{\mathrm{x}}(\mathbf{r})$], the density response function $\chi(\mathbf{r},\mathbf{r}')$, and the right-hand side of the OEP equation $b(\mathbf{r})$. (As in the later part of Ref. [1], we have dropped the subscript v.) The OEP equation $\int \chi(\mathbf{r},\mathbf{r}')v(\mathbf{r}')d\mathbf{r}' = b(\mathbf{r})$ becomes a matrix equation $\chi v = b$ in this basis, which decouples after unitary transformation to the basis of eigenfunctions $\{c^{\alpha}(\mathbf{r})\}$ of χ with eigenvalues g^{α} [21] and becomes a defining equation for the OEP $v(\mathbf{r}) = \sum_{\alpha} v_{\alpha} c^{\alpha}(\mathbf{r})$ with $v_{\alpha} = b_{\alpha}/g^{\alpha}$ and $b_{\alpha} = \int c^{\alpha}(\mathbf{r})b(\mathbf{r})d\mathbf{r}$. (In contrast to Ref. [1], we leave out the factor $-1/2$ in the definitions of g^{α} and b_{α}.) Here, one has to omit one of the eigenvalues, which is exactly zero. This null eigenvalue comes from the fact that a change in the potential by a mere constant does not affect the electron density. So, the OEP is defined uniquely only up to an insignificant constant. From the Hohenberg-Kohn theorem, it follows that all other eigenvalues of the exact χ are nonzero. (We note that all eigenvalues of the density response function are negative. When we speak of "small eigenvalues" here and in the following, we refer to their absolute values.)

III. BASIS-SET BALANCE

It has been pointed out by many authors [12–20] that the solution of the OEP equation in finite basis sets requires that the orbital and auxiliary sets are *balanced*. Otherwise, the OEP shows pathological behavior.

Gidopoulos and Lathiotakis remark that there was a "lack of definition of balanced basis sets." We must concede that the naming is, in fact, somewhat misleading as it insinuates that the basis sets had to meet some form of delicate balance condition. In fact, it is much simpler than that. The term basis-set balance refers to the *order of convergence* of the two basis sets: For a given auxiliary basis, converge the orbital basis set, then improve the auxiliary basis, and converge the orbital basis again, and so on. (So, *nested convergence* would be a more appropriate naming.) The objective here is to ensure that the density response function, a central ingredient of the OEP equation, is sufficiently accurate to obtain a well-behaved OEP. Thus, the basis-set balance is clearly defined, and it is achieved in a rather technical way following the simple scheme above.

The balance condition is a consequence of the definition of $\chi(\mathbf{r},\mathbf{r}')$ as the functional derivative $\delta n(\mathbf{r})/\delta v(\mathbf{r}')$. While the denominator is represented in the auxiliary basis, the numerator is ultimately represented in the orbital basis since the electron density is the sum of the absolute squares of the orbital functions. Thus, the orbital basis must be sufficiently flexible to enable the electron density to follow the changes applied to the potential in the denominator, which may be proportional to any of the $\xi_k(\mathbf{r})$'s. An underconverged χ exhibits eigenvalues that are typically too small. Inversion of χ then yields too large values, which eventually gives rise to pathological behavior in the OEP. This explains the order of convergence prescribed by the condition of basis-set balance.

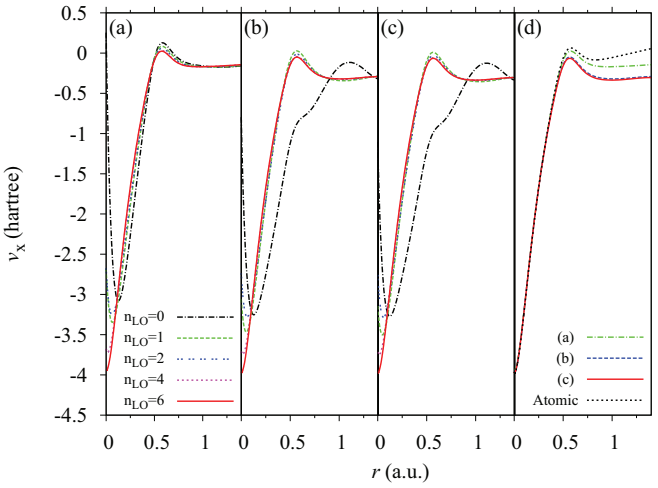

FIG. 1. (Color online) Illustration of the *balanced* convergence of the exchange part $v_x(\mathbf{r})$ of the OEP, shown here close to the nucleus at $r = 0$ and in the direction of the nearest neighbor in bulk diamond. (a)–(c) show the orbital basis convergence for three auxiliary basis sets of increasing size employing angular momentum cutoffs $l = 0$, $l \leqslant 3$, and $l \leqslant 4$, respectively; the curves correspond to different orbital basis sets where the parameter n_{LO} denotes the quality of the basis. (d) shows the overall convergence of the converged curves of (a)–(c) (dashed-dotted, dashed, and solid lines, respectively) with respect to the auxiliary basis. The exact atomic local exchange potential, shown as the black dotted line, is shifted vertically to align with the crystal exchange potentials, whose zero energy is defined by the condition $\int v_x(\mathbf{r})d\mathbf{r} = 0$.

In Fig. 1, we illustrate the convergence with balanced basis sets for the case of bulk diamond [22] employing the all-electron full-potential linearized augmented-plane-wave (FLAPW) method as realized [20] in the FLEUR code [23]. We have employed three different auxiliary basis sets using different cutoffs for the angular momentum $l = 0$, $l \leqslant 3$, and $l \leqslant 4$ (due to symmetry, $l = 1$ and $l = 2$ do not contribute) and show the convergence of the exchange part $v_x(\mathbf{r})$ of the OEP in terms of the orbital basis in Figs. 1(a)–1(c). The quality of the orbital basis is denoted by the number of local orbitals n_{LO}; see Ref. [20] for the exact definition of the basis sets. Clearly, for each auxiliary basis, the local exchange potential can be converged in terms of the orbital basis. We also observe that the more accurate the auxiliary basis is, the more expensive the orbital basis convergence becomes. In Fig. 1(d), we show the convergence of $v_x(\mathbf{r})$ with respect to the auxiliary basis, compiling the converged curves of (a)–(c). We also plot the exact atomic local exchange potential calculated with the RELKS code [24] for comparison. The latter and the converged potentials are indistinguishable close to the atomic nucleus and start to deviate noticeably at a distance of about 0.4 bohr from the nucleus where the crystal field starts to make itself felt. We note that the converged potential is smooth and does not show any sign of pathological behavior. This observation is general and applies to all materials we have examined so far [20,25,26].

IV. NONANALYTICITY

The authors of Ref. [1] give a mathematical proof that the OEP can show nonanalytic behavior when calculated in a finite basis, which we recapitulate here briefly. We consider a complete infinite auxiliary basis, whereas the orbital basis is finite, which leads to a finite number of virtual states. Since density fluctuations are generated by excitations from occupied into virtual states, only a finite number of eigenvalues of the density response function will be nonzero. The space spanned by the eigenfunctions with nonzero eigenvalues is necessarily incomplete, and we may decompose the exact quantities as $\chi = \chi_0 + \tilde{\chi}$ and $b = b_0 + \tilde{b}$, where χ_0 and b_0 are calculated with the finite orbital basis. Now, we introduce the scaled OEP equation $\chi^\lambda v^\lambda = b^\lambda$ with $\chi^\lambda = \chi_0 + \lambda\tilde{\chi}$ and $b^\lambda = b_0 + \lambda\tilde{b}$, whose solutions for $\lambda = 1$ and $\lambda = 0$ correspond to the exact OEP and that obtained with the finite orbital basis, respectively. Elimination of the null space before inversion of χ is implicit, which, in the case of χ_0, effectively reduces the infinite auxiliary basis to a finite one with maximally as many functions as there are virtual transitions from occupied to unoccupied states.

The authors then proceed to prove that $v^\lambda(\mathbf{r})$ is nonanalytic at $\lambda = 0$, i.e., $v^{\lambda\to 0}(\mathbf{r}) - v^0(\mathbf{r})$ does not vanish, in general. So, a difference must be expected between the finite-basis solution $v^0(\mathbf{r})$ and $v^{\lambda\to 0}(\mathbf{r})$, which should be closer (but not identical) to the exact result $v(\mathbf{r}) = v^1(\mathbf{r})$. The fact that $v^{\lambda\to 0}(\mathbf{r}) - v^0(\mathbf{r})$ can be nonzero is obvious by realizing that the two potentials are defined differently: $v^{\lambda\to 0} = \lim_{\lambda\to 0}[(\chi^\lambda)^{-1}b^\lambda]$ and $v^0 = \lim_{\lambda\to 0}[(\chi^\lambda)^{-1}(\lim_{\lambda\to 0} b^\lambda)]$, which clearly are mathematically

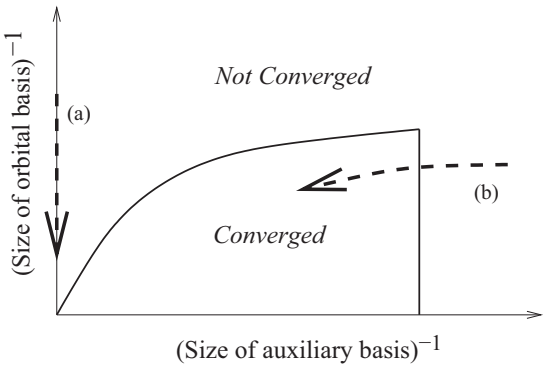

FIG. 2. Illustration of the qualitative convergence behavior of the OEP. The line surrounding the converged regime corresponds to a predefined convergence tolerance. Increasing the orbital basis with respect to an infinite auxiliary basis (a) never leads to convergence, whereas the path (b) represents convergence with balanced basis sets.

different expressions that will, in general, evaluate to different potentials. Gidopoulos and Lathiotakis give an explicit formula for the discontinuity $v^{\lambda\to 0} - v^0$ in Eq. (28) of their paper.

The way basis-set convergence is performed above—the orbital basis is converged against an infinite auxiliary basis—is clearly the extreme opposite of basis-set balance. Figure 2 shows an illustration. The balance condition guarantees that the matrix elements of the density response function are sufficiently accurate in each step of the auxiliary basis convergence. In the wording of Ref. [1], converging the orbital basis in this way *pushes* the null space out of the space spanned by the auxiliary basis. The potential is, thus, found by increasing the auxiliary basis until convergence of $v(\mathbf{r})$ is reached, whereas the orbital basis is always chosen large enough to ensure a well-converged density response matrix. An insufficiently converged density response function, on the other hand, would introduce a finite error that eventually precludes convergence with respect to the auxiliary basis or leads to convergence to an unphysical result.

With balanced basis sets, the only parameter left is the size of the auxiliary basis (while the orbital basis is chosen to fulfill the basis-set balance). It is easy to see that the nonanalyticity disappears for a potential $v^0(\mathbf{r})$ that is converged in this way: Convergence means that $v^0(\mathbf{r})$ also solves the OEP equation for an auxiliary basis that is augmented by an arbitrary function $\xi^\nu(\mathbf{r})$ from the orthogonal space [27], which implies $\sum_\alpha \chi_{\nu\alpha} v^0_\alpha = b_\nu$ (and $\sum_\alpha \tilde{\chi}_{\nu\alpha} v^0_\alpha = \tilde{b}_\nu$). Extending this to all ν's yields $v^0 = v^{\lambda\to 0}$ after insertion into Eq. (28) of Ref. [1] and implies $v^0 = v^1$. One might suspect that the assumption that $v^0(\mathbf{r})$ is a converged potential already implies the final result. This is not so since numerical convergence is no guarantee that the converged quantity equals the exact result. An example of such a *false convergence* is shown in Fig. 2 of Ref. [1].

V. ROLE OF SMALL EIGENVALUES

According to experience [19,20], a proper convergence of the density response matrix using balanced basis sets is sufficient to obtain a nonsingular χ, i.e., a χ that does not exhibit numerically small eigenvalues, which would otherwise preclude a straightforward matrix inversion. Too small eigenvalues can be caused by an underconverged orbital basis, i.e., the electron density cannot sufficiently follow the potential variations, and can give rise to pathological behavior in the final potential. We briefly discuss the simple case of the homogeneous electron gas to show that the physical χ, when represented in a finite basis, is expected to be far from a singular matrix. In this case, the density response function $\chi(\mathbf{q})$ is given by the $\omega \to 0$ limit of the analytic Lindhard function, whose monotonically decreasing absolute value approaches zero with a q^{-2} asymptote. Given that the number of plane waves (which are the eigenfunctions in this case) grows as $N \sim q^3$, we find that $\chi \sim N^{-2/3}$. A similarly slow decrease is expected for the eigenvalues of χ in the inhomogeneous case. In fact, we have found eigenvalues not smaller than 10^{-3} in the systems studied so far, whereas in Ref. [1] eigenvalues below 10^{-10} are reported, which indicates that the orbital basis was not properly converged.

Instead of a systematic convergence of the orbital basis, Gidopoulos and Lathiotakis approach the problem differently. First, they define the null space of χ, which is spanned by eigenfunctions of χ with eigenvalues smaller than a cutoff $g_{\min}$ (they use $g_{\min} = 1.04 \times 10^{-3}$). In their words, the corresponding eigenfunctions span the null space of χ along which the OEP is undetermined. They eliminate the null space from the basis and solve the OEP equation in the reduced basis. This is known as singular-value decomposition. The resulting potential $v^0(\mathbf{r})$ shows pathological behavior (Fig. 2 of their paper). Then, they add a correction $\bar{v}(\mathbf{r})$ for the omission of the null space (Fig. 3 of their paper), which is defined as an approximation to the discontinuity $v^{\lambda\to 0}(\mathbf{r}) - v^0(\mathbf{r})$ and propose $v^0(\mathbf{r}) + \bar{v}(\mathbf{r})$ as the corrected OEP. However, the correction requires careful classification of the eigenvalues of the response function into singular and nonsingular eigenvalues, a classification that the authors themselves admit to be an "ill-posed" problem. Otherwise, the resulting potential exhibits spurious oscillations around

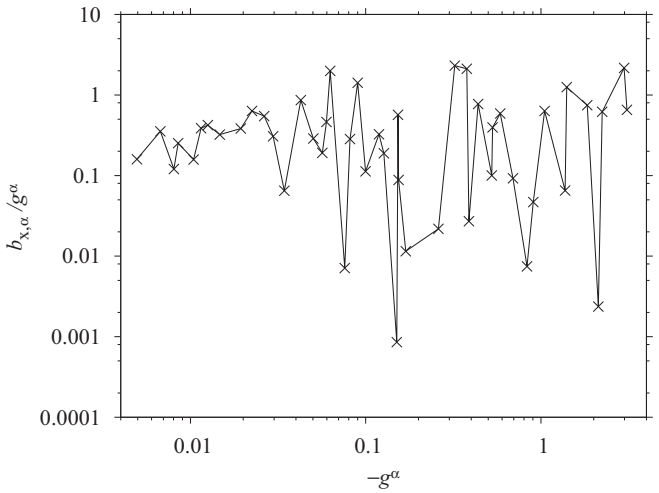

FIG. 3. Fraction $v_{x,\alpha} = b_{x,\alpha}/g^\alpha$ for all contributing eigenfunctions $c^\alpha(\mathbf{r})$, i.e., those for which $b_{x,\alpha} \neq 0$, as a function of the eigenvalue g^α for CoTiSb using balanced basis sets. The importance of the contributions $v_{x,\alpha}$ is clearly not related to g^α, i.e., small eigenvalues of χ can give important contributions to $v_{x,\alpha}$.

the exact potential. This becomes particularly obvious in the potential v_x^* shown in Fig. 5(b) of Ref. [1], which shows the effect of transferring an additional eigenvector from the null space into the effective nonsingular space by slightly decreasing the threshold $g_{\min}$: Additional strong oscillations appear.

We attribute this behavior to the only approximate treatment of the small eigenvalues of χ, which is based on the misconception that they were unimportant. This is not so. The OEP is constructed from $v_\alpha = b_\alpha/g^\alpha$, i.e., even if g^α is small, the numerator b_α could be equally small, which would make the fraction nonsingular. In fact, we often observe this behavior and show, as an illustration in Fig. 3, the exchange contribution of $v_\alpha = b_\alpha/g^\alpha$, i.e., $b_{x,\alpha}/g^\alpha$, as a function of the eigenvalues g^α for the case of CoTiSb. Evidently, the importance of the eigenfunctions, quantified by the y coordinate, does not scale with the size of the eigenvalues. Small values of g^α tend to cancel with equally small values of b_α in the ratio b_α/g^α. This behavior is consistent with the underlying OEP equation and seems to be valid in a quite general sense in our experience. Another point to mention here is that an underconverged orbital basis does not only affect the small eigenvalues adversely but the whole eigenvalue spectrum (see Fig. 6 in Ref. [20]). So, even if the Unsöld approximation worked well for the small eigenvalues, there would still be no correction for the rest of the eigenspectrum, which will inevitably lead to inaccuracies in the OEP.

Often, the establishment of the basis-set balance can be rather cumbersome numerically. Recently, we published [25,26] an incomplete-basis-set correction (IBC), which facilitates the fulfillment of the balance condition considerably. Although basis-set balance is still a necessary condition, the IBC effectively accelerates the convergence of χ to such an extent that converged OEPs are obtained already with standard orbital basis sets, routinely employed in density-functional-theory calculations using simple local or semilocal functionals. This decreases the computational demand considerably. To some extent, it incorporates an infinite number of unoccupied states. It is important to note that both procedures, with and without the IBC, converge to the exact OEP. In the atomic limit, it can even be shown to yield the *exact* OEP, which is used as a reference in Ref. [1], provided that the atomic spheres used in the FLAPW method are made large enough to accommodate all occupied atomic orbitals.

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We acknowledge helpful discussions with A. Görling about the condition of basis-set balance.

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